

FORM PTO-1390 (REV. 10-94)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 71272
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			08/913976
INTERNATIONAL APPLICATION NO. PCT/AU96/00189	INTERNATIONAL FILING DATE 02 April 1996	PRIORITY DATE CLAIMED 05 April 1995	
TITLE OF INVENTION OIL FOR AGRICULTURAL USE			
APPLICANT(S) FOR DO/EO/US Mark HODGKINSON			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11. to 16. below concern document(s) or information included:			
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input checked="" type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: 			
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U S APPLICATION NO. (If known, see 37 C.F.R. 1.5)		INTERNATIONAL APPLICATION NO PCT/AU96/00189		ATTORNEY'S DOCKET NUMBER 71272	
				CALCULATIONS PTO USE ONLY	
<p>17. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</p> <p>Search Report has been prepared by the EPO or JPO \$910.00</p> <p>International preliminary examination fee paid to USPTO (37 CFR 1.482) \$700.00</p> <p>No international preliminary examination fee paid to USPTO (37 CFR 1.482), but international search fee paid to USPTO (37 CFR 1.445(a)(2)) . . . \$770.00</p> <p><input checked="" type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1040.00</p> <p>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00</p> <p style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</p>					
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest priority date (37 CFR 1.492(e)).				\$ 130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	16 -20=	0	x \$22.00	\$.00	
Independent claims	4 -3=	1	x \$80.00	\$ 80.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ 260.00	\$.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 80.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$ 1,250.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+	
TOTAL NATIONAL FEE =				\$ 1,250.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property				+	
TOTAL FEES ENCLOSED =				\$ 1,250.00	
				Amount to be: refunded	\$
				charged	\$
<p>a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1,250.00</u> to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0920</u>. A duplicate copy of this sheet is enclosed.</p> <p>NOTE. Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO: WELSH & KATZ, LTD. 120 South Riverside Plaza 22nd Floor Chicago, Illinois 60606 Telephone: 312/655-1500</p> <p style="text-align: right;"><u>Gerald T. Shekleton</u> SIGNATURE <u>Gerald T. Shekleton</u> NAME <u>27,466</u> REGISTRATION NUMBER</p>					

08/913976

Revised PCT/PTO 25 SEP 1997

71272

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re U.S. Patent Application

) Art Unit: Not Yet Assigned

Applicant: Mark HODGKINSON

Serial No.: Not Yet Assigned

Filed: Not Yet Assigned

For: **OIL FOR AGRICULTURAL USE**

Examiner: Not Yet Assigned

-not used for fee
calculation
- refers to claims
superseded by
Art 34 amendment

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

This is a Preliminary Amendment for entry in the above-identified application.

IN THE SPECIFICATION:

Please substitute new pages 3-5 for those originally filed in the international patent application. A substitute specification is enclosed with these pages substituted.

IN THE CLAIMS:

Please delete Claims 1-21.

Please add new Claims 22-37 as follows:

---22. An agricultural spray oil having added thereto an oil soluble basic compound that is selected from the group consisting of:

- (a) a sulphonate;
- (b) a phenate; and

5 (c) an alkyl-amine.

23. An agricultural spray oil as claimed in Claim 22, wherein the sulphonate is an overbased sulphonate and the phenate is an overbased phenate.

24. An agricultural spray oil as claimed in Claim 23, wherein the overbased sulphonate is a calcium overbased sulphonate.

25. An agricultural spray oil as claimed in Claim 24, wherein the calcium overbased sulphonate is present in the oil in a range of 0.01-5.0 wt% total.

26. An agricultural spray oil as claimed in Claim 25, wherein the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total.

27. An agricultural spray oil having added thereto an oil soluble UV deactivator that is selected from the group consisting of:

(a) a benzotriazole UV absorber;

(b) a zinc diamyldithio carbamate; and

5 (c) a benzoxazole, benztriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

28. An agricultural spray oil as claimed in Claim 27, wherein in (a) the UV absorber is:

- (i) TINUVIN 171; or
- (ii) iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate.

29. An agricultural spray oil as claimed in Claim 28, wherein compound (ii) is present in the range of 0.001-0.5 wt% total.

30. An agricultural spray oil as claimed in Claim 28, wherein compound (i) is present at about 0.005 wt% total; or compound (ii) is present at about 0.1 wt% total.

31. An agricultural spray oil as claimed in Claim 22, wherein the oil portion is a C₁₅ to C₃₅ light paraffinic petroleum-derived oil or a C₁₅ to C₃₅ light naphthenic petroleum-derived oil.

32. An agricultural spray oil as claimed in Claim 31, wherein the light paraffinic oil or light naphthenic oil is:

- (a) chemically neutralized;
- (b) clay treated;
- (c) solvent refined; or
- (d) hydro-treated.

33. An agricultural spray oil as claimed in Claim 22, further including an emulsifying surfactant.

34. An agricultural spray oil as claimed in Claim 33, wherein the surfactant is nonionic surfactant and is added at about 0.5 wt% to 20.0 wt% total of the oil.

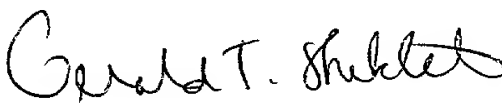
35. An agricultural spray oil including an oil soluble basic compound selected from the group consisting of (a) a sulphonate; (b) a phenate; and (c) an alkyl-amine and a UV deactivator selected from the group consisting of (a) a benzotriazole UV absorber; (b) a zinc diamyldithio carbamate; and (c) a benzoxazole, benztriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

36. An additive composition for an agricultural spray oil including a base selected from the group consisting of (a) a sulphonate; (b) a phenate; and (c) an alkyl-amine and a UV deactivator selected from the group consisting of (a) a benzotriazole UV absorber; (b) a zinc diamyldithio carbamate; and (c) a benzoxazole, benztriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

37. The additive composition of Claim 36, having an oil portion of a C₁₅-C₃₅ light paraffinic petroleum-derived oil or C₁₅ to C₃₅ light naphthenic-derived oil and an emulsifying surfactant.---

Respectfully submitted,

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OIL FOR AGRICULTURAL USEFIELD OF THE INVENTION

5 The present invention relates to an oil for agricultural use, in particular to a petroleum derived spray oil "PSO", being primarily an oil for use as an insecticide and/or an acaricidal control spray oil. More particularly, the invention relates to a PSO having certain additive(s) which reduces the phytotoxicity of the oil in relation to, for example, crops and plants.

10 The invention will be primarily described in relation to its use with refined and semi-refined light oils, but it should be appreciated that the invention has broader application.

BACKGROUND ART

15 Petroleum spray oils ("PSO's") are used in agriculture on their own and as carriers or solvents for spraying pesticides, herbicides, micronutrients, chemical adjuvants, etc. The oils are widely used because of their effectiveness in controlling a wide range of pests

20 and diseases, and because of their relatively low cost, relatively low health hazard (including low mammalian toxicity) and wide availability. They also show an absence of residual effect against beneficial predators and parasitoids.

25 However, certain grades and applications of PSO's have been shown to be phytotoxic, particularly in high dosage applications, or in environments where exposure to sunlight is imminent or intense. Acute phytotoxicity can lead to excessive leaf drop in plants and less obvious

30 chronic symptoms such as inhibition of yield of crops.

There has been much debate in the scientific literature as to the mechanisms of oil induced

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phytotoxicity, but a primary source of phytotoxicity has been attributed to membrane disruption. Membrane disruption involves the dissolution of folia semipermeable membranes, leading to a breakdown in the plant structure and wilting and/or death of the plant. The problem of membrane disruption was largely overcome by improved oil refinement and the instigation of quality criteria.

Phytotoxic effects have been linked with the distillation temperature or viscosity of the particular oil used in spraying. Phytotoxicity has also been attributed to spray oil dose rate and duration of spraying.

However, photodegradation of modern highly refined PSO's with subsequent phytotoxicity has largely been overlooked by researchers and manufacturers in this area.

The formation of acids in PSO's is associated with the photo-degradation (eg. oxidation) of the PSO mediated by UVA radiation. It is now surmised that a contributing or major factor in the phytotoxicity of PSO's could relate to the level of acidity in the PSO when sprayed, or developed after spraying. Even "superior" spray oils (ie. highly refined spray oils), upon exposure to light, may develop acidity and become markedly phytotoxic. This tendency can be enhanced where an oil applied to a plant is exposed to UV radiation (eg. sunlight) for an extended period of time, so that many of the components of the oil are photo-oxidised into organic acids, in turn attacking the plants.

It would be advantageous if at least preferred embodiments of the present invention provided an oil for agricultural use, in particular an oil for agricultural spraying, that includes therein a component, or components, capable of preventing the formation of acidic products within the oil, or ameliorating or neutralising their effects.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides an agricultural spray oil having added thereto an oil soluble basic compound that is selected from one or more
5 of:

- (a) a sulphonate;
- (b) a phenate;
- (c) an alkyl-amine.

By employing such an oil soluble basic compound, at
10 least some of any acidic compounds present in or formed in the oil in use can be neutralised.

Preferably the sulphonate and phenate are respectively overbased sulphonates or phenates, and it is particularly preferred that the sulphonate is a calcium
15 overbased sulphonate.

Preferably, the calcium overbased sulphonate is present in the oil in a range 0.01-5 wt% total. It is most preferred that the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total.
20 A metal overbased sulphonate includes an aqueous micelle defined by a plurality of relatively long-hydrocarbon chain molecules having a polar head (ie. sulphonate functionality) and a hydrophobic tail (eg. long chain alkyl) and an excess amount of metal base (eg. calcium
25 carbonate) in the micelle. (A depiction of an overbased sulphonate is shown in Figure 5). Metals other than calcium can also be used in the sulphonate or phenate (eg. magnesium overbased sulphonates).

As described above, exposure of a PSO to UV
30 radiation brings about photo-degradation of the PSO (ie. through the photo-oxidation thereof) into peroxides, acids, esters, polymers etc, thus increasing the phytotoxicity of the PSO.

In a second aspect, the present invention provides
35 an agricultural spray oil having added thereto an oil

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soluble UV deactivator that is selected from one or more of:

- (a) a benzotriazole UV absorber;
- (b) a zinc diamyldithio carbamate; or
- 5 (c) a benzoxazole, benztriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

Photo-oxidation can thus be prevented or ameliorated, or alternatively any photo-oxidation
10 products (eg. peroxide free-radicals) may be scavenged and/or trapped.

The UV absorber absorbs UV radiation and thus tends to prevent photo-oxidation, whereas the free-radical trap or scavenger neutralises any free-radicals produced
15 during photo-oxidation (eg. peroxides).

Preferably, the UV absorber is TINUVIN 171, pref. at 0.005%. (Trade mark of Ciba Geigy).

Alternatively, the UV absorber can be iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl)
20 propionate. (A commercially available form of this compound is known as TINUVIN 384 (Trade Mark of Ciba Geigy Limited). TINUVIN 384 is a liquid UV absorber of the hydroxyphenyl benztriazole class. It has high thermal stability and permanence.

Preferably, the iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate is present
25 in the range of 0.001-0.5 wt% total of the oil, most preferably at about 0.01 wt% total of the oil.

The free-radical trap or scavenger is zinc
30 diamyldithiocarbamate.

A preferred oil for use as a PSO is a refined light oil (C₁₅ to C₃₅ length of hydrocarbon chain). In particular, it is preferred that the oil portion of the PSO is a C₁₅ to C₃₅ light paraffinic or light naphthenic
35 petroleum derived oil.

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Preferably, the light paraffinic or light naphthenic
boil is:

- (a) chemically neutralised;
- (b) clay treated;
- 5 (c) solvent refined; or
- (d) hydro-treated.

Physical properties of such oils are shown in Tables
2 and 3.

10 Surfactants are typically added to PSO's to enable
the oil to be dispersed in water for subsequent spraying.
Typical surfactants include nonionic surfactants. The
nonionic surfactants can be added in the range of 0.5 wt%
to 20 wt%.

15 In a most preferred spray oil formulation, a refined
light oil can include 0.5 - 20 wt% nonionic surfactant,
1.0 wt% calcium overbased sulphonate and 0.005 wt%
benztriazole compound. Thus, preferred formulations may
include both an oil soluble basic compound and a UV
deactivator.

20 In a further aspect of the present invention an
additive composition for an oil for agricultural use is
provided which can include a base (as defined above),
and/or a UV deactivator (as defined above).

25 This additive composition can also include
emulsifying surfactant(s) (as defined above). Such an
additive composition can be provided separately from the
oil (eg. PSO) and can be added to the oil in situ (eg.

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prior to spraying). The additive composition finds useful application when added to less than ideally refined oils, or oils that are in various stages of oxidation, and can stabilise, eliminate or reduce the phytotoxicity of such oils prior to spraying etc.

BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example, and also in conjunction with the attached Figures in which:

Figure 1 shows the effect of acidity on betacyanin efflux and the control thereof by adding calcium overbased sulphonate to oils (with reference to oils without such addition);

Figures 2 and 4 show the effect of adding a base and UV deactivator to different oils when exposed to UV radiation;

Figure 3 shows a fourier transform infra-red carbonyl peak measurement (ie. measurement of acidity) for different oils with base and/or UV deactivator added thereto;

Figure 5 depicts schematically typical molecular structures of sulphonates and phenates;

Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones (as preferred UV deactivators);

Figure 7 shows schematically the molecular structure of TINUVIN 384; and

Figure 8 shows the transmission spectrum for various solution concentrations of TINUVIN 384 in toluene.

MODES FOR CARRYING OUT THE INVENTION

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Some non-limiting examples of preferred embodiments of the invention will now be described.

EXAMPLES

A standard nomenclature has been employed throughout the examples for the petroleum spray oils. For example, when a PSO is referred to as a 60N or 70N oil, the number portion refers to and is derived from the measurement of viscosity in Saybolt universal seconds and the term neutral (N) refers to the paraffinic nature of the oil.

When the terminology ASTM and AS is used throughout the specification it is a reference to American Society for Testing and Materials and Australian Standard respectively.

Membrane disruption (and thus phytotoxicity), as referred to in the Figures has been measured by the Betacyanin Efflux Test. The standard test is applied on beetroot tuba disks which have no cuticle and thus the effects of a PSO on the cell membrane can be monitored directly.

MEMBRANE DISRUPTION BY BETACYANIN EFFLUX FROM UNPROTECTED CELL MEMBRANES

Oil induced disruption of cell membranes unprotected by a cuticle layer was measured by betacyanin efflux from beetroot tuba disks (Coupland, D. et al. (1989) Evaluation of three techniques used to determine surfactant phytotoxicity; Annals of Applied Biology 115, 147-156). Test material was prepared by making 7 mm diameter disks with a cork borer and cutting them to 1 mm thickness. Preliminary studies showed disks were best used after a two hour rinse in tap water followed by air drying. It was essential to remove adsorbed water because water induced premature betacyanin efflux.

Dry disks (n=3) of known fresh weight were added to 10 mL test tubes and completely covered by 2 Ml oil. The

treatments were then incubated for 3 hours at 30°C when an isotonic solution of 5 Ml of 0.4 M sorbitol in deionised water was added. The tubes were set aside to allow betacyanin efflux for 18 hours at 20°C. Analysis of the aqueous layer was performed by colorimetric analysis at 535 nm in 1 cm cells against a solvent blank. Absorbance readings were then normalised to absorbance/disk weight to eliminate differences between disks. This procedure together with the choice of three randomly chosen disks was successful in obtaining reproducible results. Cooking of the disks to produce a maximum efflux for normalisation purposes did not improve the precision.

The pink colour developed by betacyanin efflux conformed to a classical logistic curve when calibrated with oil acidity. The effective dose (ED₅₀) for 3 hours contact was 0.11 mg KOH/g oil (ASTM D927) and the detection limit for no observable effect was 0.08 mg KOH/g oil (0.5 Abs units/g).

In the Figures and Tables, the phytotoxicity of various spray oils, as determined by betacyanin efflux, is shown.

From the tests, it was established that when a membrane disruption value of 0.5 Absorbance Units/g specimen (Abs/g) was exceeded, then damage to the plant would follow. In other words, a result of 0.5 or less is a phyto-safe membrane disruption value.

Example 1 (Figure 1)

Various levels of calcium overbased sulphonate, (shown as "base" in Figure 1) were added to 70N and 150N oils, both oxidised and unoxidised. As shown clearly in Figure 1, with the addition of both 0.1% of the base and 1% of the base, the membrane disruption value is held below about 0.4 Abs/g (which is in the phyto-safe zone). Figure 1

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also compares these oils against standard oils of different acid values.

Example 2 (Figure 2)

5 A 70N oil had a number of additives (as shown in Figure 2) added thereto. Figure 2 shows the effects of exposing the oil to 4mW of UV radiation/cm² with time, and also indicates the effects of variation in the levels of base (eg. calcium overbased sulphonate) and UV deactivator (eg. TINUVIN 384).

10 Example 3 (Figure 3)

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A 70N oil (with similar additives to Example 3) was exposed to 4mW of UV radiation/cm². Figure 3 shows the results from a fourier transform infra-red spectrum of the oil with time, indicating the variation in acidity between various "treated" and "untreated" oils. From Figure 3, it can be seen that the addition of even a small amount of base and UV deactivator minimises the formation of acids (indicated by the carbonyl function, ie. absorbance at 1710 cm⁻¹).

20 Example 4 (Figure 4)

In a similar manner to Example 2, a 70N oil had a number of additives added thereto and was then exposed to UV radiation. The acidity of the resultant oil with time is shown for various combinations of the base and UV
25 deactivator, indicating that excellent results are obtained when both a base and a UV deactivator are present.

Example 5

30 Various additive compositions for use as a separate additive or concentrate pack for addition to oils for agricultural use were prepared. The additive compositions most typically included one or two nonionic

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surfactants (ie. emulsifying surfactants to render the oil suitable for use as a PSO (eg. in water)), and an oil soluble base (eg. calcium overbased sulphonate) and/or a UV deactivator (eg. TINUVIN 384).

5 An advantage of an additive composition is that it can be added to PSO's in situ (ie. it can be transported in a concentrate form to the user of the PSO, who then adds an appropriate dosage). This means that a local or regional oil can be employed (ie. the treated oil itself
10 does not need to be transported to site) and thus transportation costs can be reduced.

 A most preferred additive composition was as follows: Nonionic surfactant(s) plus calcium overbased sulphonate and benztriazole compound in a ratio of
15 140.5:1, (not including surfactant).

Example 6

Another preferred formulation for a light petroleum spray oil included 0.5 - 20 wt% nonionic surfactant, 1.0 wt% calcium overbased sulphonate and 0.05 wt% TINUVIN 384.

20 Table 1 below summarises the photo-degradation performance of various compositions when added to 60 Neutral oil, 70 Neutral oil and 150 Neutral oil, against these oils by themselves. This Table demonstrates the broad applicability of the formulation in different types
25 of oil, and shows that membrane disruption and acidity are considerably reduced or eliminated when such additives are present.

 Table 2 shows the typical chemical characteristics of petroleum spray oils suitable for use with the present
30 invention. Table 3 shows some of the properties of a broad range of light spray oils suitable for use in the present invention. Table 4 shows absorption spectra of a

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number of different benzophenones for use as a UV deactivator.

Figure 5

Figure 5 shows a schematic representation of the typical molecular structures of overbased sulphonates and phenates, wherein the micelle is defined by a plurality of water-soluble polar sulphonate functionality groups (hydrophilic heads) facing inwardly, with each sulphonate head having an oil soluble non-polar alkyl chain (hydrophobic tail) projecting outwardly therefrom.

The overbased sulphonates contain an excess amount of metal base (eg. calcium carbonate) which neutralises acids formed during photo-degradation of the oils. The alkyl chain length of the sulphonates ranges from 18 to over 20 carbon atoms, whereas the alkyl chain length of the phenates contains approximately 12 carbon atoms.

Figures 6, 7 and 8

Figure 6 shows the UV absorption spectra of typical 2-hydroxybenzophenones which can be used as a UV deactivator in some forms of the present invention. (Table 4 also shows the absorption spectra of different benzophenones).

Figure 7 shows the chemical structure of TINUVIN 384 and

Figure 8 shows a transmission spectra for various concentrations of TINUVIN in toluene, indicating its preferred usage as a UV absorber.

From the above description, it can be seen that the addition of an oil soluble base and an oil soluble UV deactivator (in various preferred configurations) can eliminate, ameliorate or reduce membrane disruption (as

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10

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TABLE 1
THE EFFECT OF ADDITIVES IN PETROLEUM SPRAY OIL

Treatment exposed for 20 hours [0.2mW/cm ² UV [a] light]	Belacyanin efflux (Abs/g)	Carbonyl peak (Abs. units)	Acidity mg KOH/g
60 Neutral oil	2.45	0.1209	0.26
60 Neutral oil + 1% base +0.005% UV deactivator	0	0.0678	0.009
70 Neutral oil	3.16	0.1421	0.3
70 Neutral oil + 1% base +0.005% UV deactivator	0	0.0858	0.007
150 Neutral oil	2.57	0.2118	0.77
150 Neutral oil + 1% base +0.005% UV deactivator	0	0.1395	0.26

TABLE 2

TYPICAL CHEMICAL CHARACTERISTICS OF PETROLEUM SPRAY OILS

Analysis	Method	Typical base oil ^A	AS 1888 C21 NR class ^B	AS 1888 C23 NR class ^B
Density @ 15°C	ASTM D1298 (g/mL)	.846	<0.870	<0.880
Refractive index @ 20°C	ASTM D1218	1.4680	-	-
Viscosity @ 40°C	ASTM D2270 (cSt)	12	-	-
%UR	ASTM D483	94	>92	>92
Carbon No. @10% ^C	Furness et al. 1987	20.2	>18.2	>19.0
Carbon No @50%	"	23.5	>21	>22.0
Carbon No. @90%	"	25.3	<24.2	<26.0
50% DT	ASTM D2887	385°C	>357°C	>369°C
50% DT	ASTM D1160	231°C	>206°C	>217°C
Boiling range	ASTM D2887	57°C	<74°C	<81°C
%Cp	ASTM D3238	70	-	-
%Cn	"	28	-	-
%Ca	"	2	-	-
%Aromatic mass	ASTM D2549	10	-	-

A = 70 Neutral

B = Proposed Australian standard [Furness et al. 1987]. These classes equate to the USA "superior" oil grade.

C = Carbon Number when X% mass has distilled.

NR = Narrow Range

%Cp = % carbon atoms as paraffin, n = naphthene, a = aromatic

DT = Distillation temperature (C°: @ 101 kPa ASTM D2887 or 10 kPa ASTM D1160).

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TABLE 3

Properties of Oils as Defined by the TSCA Inventory^A

CAS name of distillates	CAS No.	Carbon number distribution	Remarks
Chemically neutralized light paraffinic	64742-28-5	C15-C30	Contains relatively large proportion of saturates
Chemically neutralized light naphthenic	64742-35-4	C15-C30	Few normal paraffins
Clay treated light paraffinic	64742-37-6	C15-C30	Mostly saturates
Clay treated light naphthenic	64742-45-6	C15-C30	Few normal paraffins
Solvent refined light paraffinic	64741-89-5	C15-C30	Predominantly saturates
Solvent refined light naphthenic	64741-97-5	C15-C30	Few normal paraffins
Hydrotreated light paraffinic	64742-55-8	C15-C30	Contains a relatively large proportion of saturates
Hydrotreated light naphthenic	64742-53-6	C15-C30	Few normal paraffins

A: US EPA (1978); TSCA, US Toxic substances control act.

B: CAS number: Chemical abstracts service registry number.

TABLE 4

ABSORPTION SPECTRA OF BENZOPHENONES

Benzophenone (substituents)	a		b		c		Ref.
	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$	
None	250	4.30	—	—	353	1.85	89
4-OH	248	4.00	289	4.17	—	—	114
4,4'-di-OH	—	—	295	4.28	—	—	114
2-OH	251	4.04	—	—	342	3.20	89
2-OMe	251	4.04	—	—	342	3.20	89
3-OMe	256	4.05	—	—	—	—	89
2,4-di-OH	242	3.94	290	3.96	338	4.12	114
2,6-di-OH	250	4.07	280	3.74	—	—	114
2,6-di-OH-5- ϕ CO	248	4.30	290	3.90	348	4.34	114
2,4-di-OH-5- ϕ CO	258	4.27	275	4.26	338	4.15	114
2,6-di-OH-3,5-di- ϕ CO	258	4.30	280	4.53	330	3.91	114
2,4-di-OH-2'-OMe	256	4.16	285	4.29	325	4.14	114
2,4-di-OH-4'-Me	250	3.93	290	4.07	340	4.09	114
2,4-di-OH-4'-Cl	250	4.08	290	4.02	325	4.04	114
2,4-di-OH-3',4'-di-Cl	252	3.98	290	4.10	325	3.96	114
2,4-di-OH-2',4'-di-OH	242	3.80	283	3.96	352	4.17	114
2,4-di-OMe	245	4.18	280	3.86	310	3.78	114
2-OH-4-OMe	—	—	289	4.13	322	3.96	114
2-OH-4,4'-di-OMe	—	—	285	4.20	320	4.12	114
2-OH-4-OMe-3-Me	250	3.89	300	4.27	—	—	114

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CLAIMS:

1. An agricultural spray oil having added thereto an oil soluble basic compound that is selected from one or more of:

- 5 (a) a sulphonate;
 (b) a phenate;
 (c) an alkyl-amine.

10 2. An agricultural spray oil as claimed in claim 1, wherein the sulphonate is an overbased sulphonate and the phenate is an overbased phenate.

3. An agricultural spray oil as claimed in claim 2, wherein the overbased sulphonate is a calcium overbased sulphonate.

15 4. An agricultural spray oil as claimed in claim 3, wherein the calcium overbased sulphonate is present in the oil in a range 0.01-5.0 wt% total.

5. An agricultural spray oil as claimed in claim 4, wherein the calcium overbased sulphonate is present in the oil in an amount of about 1.0 wt% total.

20 6. An agricultural spray oil having added thereto an oil soluble UV deactivator that is selected from one or more of:

- (a) a benzotriazole UV absorber;
 (b) a zinc diamyldithio carbamate; or
25 (c) a benzoxazole, benzotriazole or benzthiazole compound, but excluding the compound 2-mercaptobenzothiazole.

7. An agricultural spray oil as claimed in claim 6, wherein in (a) the UV absorber is:

- 30 (i) TINUVIN 171; or

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(ii) iso-octyl-3-(3-(2H-benzotriazole-2-yl)-5-tert.butyl-4-hydroxyphenyl) propionate.

8. An agricultural spray oil as claimed in claim 7, wherein compound (ii) is present in the range of 0.001-0.5 wt% total.

9. An agricultural spray oil as claimed in claim 7, wherein compound (i) is present at about 0.005 wt% total; or compound (ii) is present at about 0.1 wt% total.

10. An agricultural spray oil as claimed in any one of the preceding claims, wherein the oil portion is a C₁₅ to C₃₅ light paraffinic or light naphthenic petroleum derived oil.

11. An agricultural spray oil as claimed in claim 10, wherein the light paraffinic or light naphthenic oil is:

- (a) chemically neutralised;
- (b) clay treated;
- (c) solvent refined; or
- (d) hydro-treated.

12. An agricultural spray oil as claimed in any one of the preceding claims, further including emulsifying surfactant(s).

13. An agricultural spray oil as claimed in claim 12, wherein the surfactant(s) are nonionic surfactant(s) and are added at about 0.5 wt% to 20.0 wt% total of the oil.

14. An agricultural spray oil including the oil soluble basic compound as defined in any one of claims 1 to 5 and the UV deactivator as defined in any one of claims 6 to 9.

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the UV deactivator as defined in any one of claims 6 to 9.

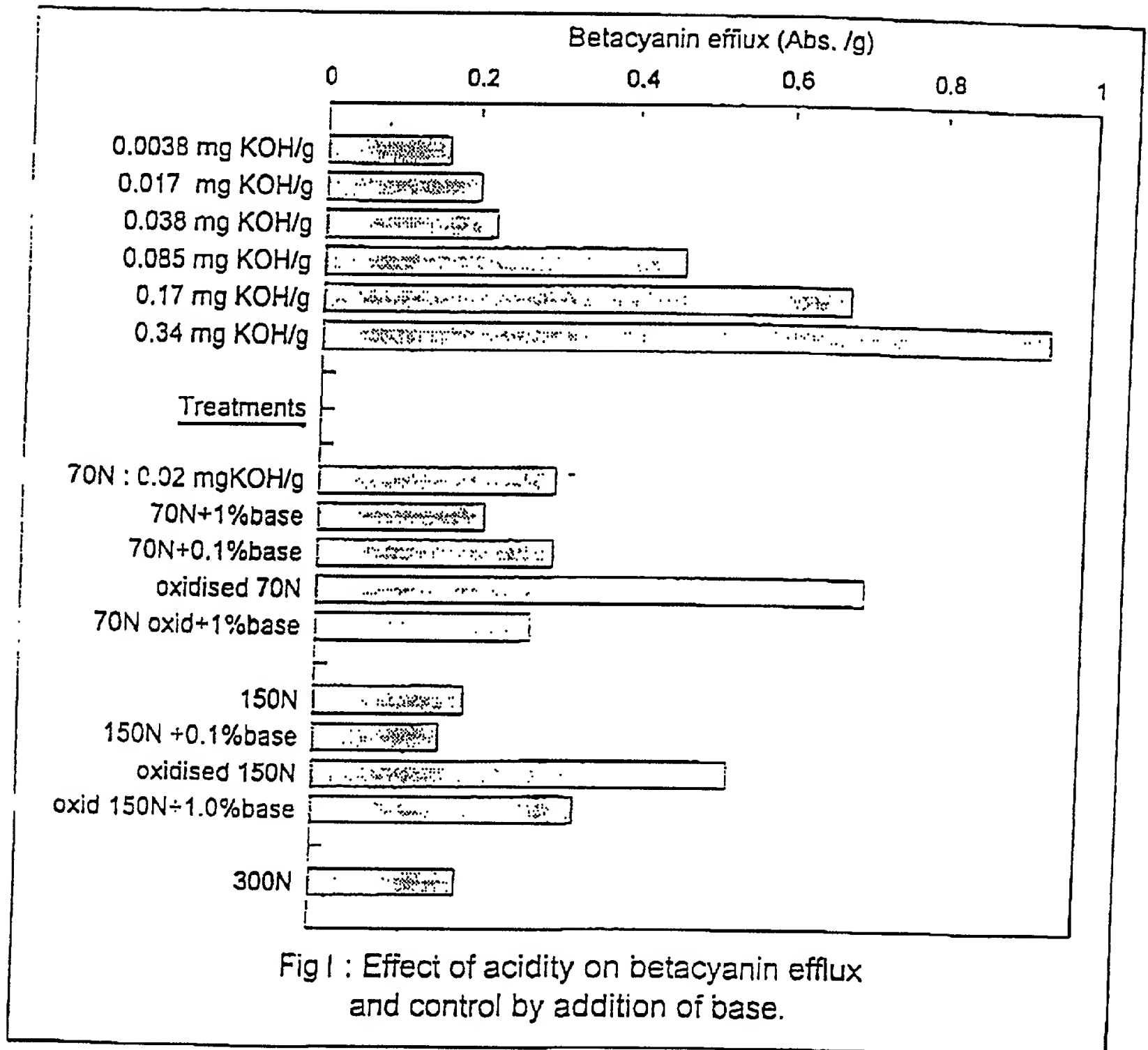
15. An additive composition for an agricultural spray oil including a base as defined in any one of claims 1 to 5 and/or a UV deactivator as defined in any one of claims 6 to 9.

16. An additive composition as claimed in claim 21, which is added to an oil as defined in claim 10 or claim 11, the additive composition optionally including emulsifying surfactant(s) as defined in claim 12 or claim 13.

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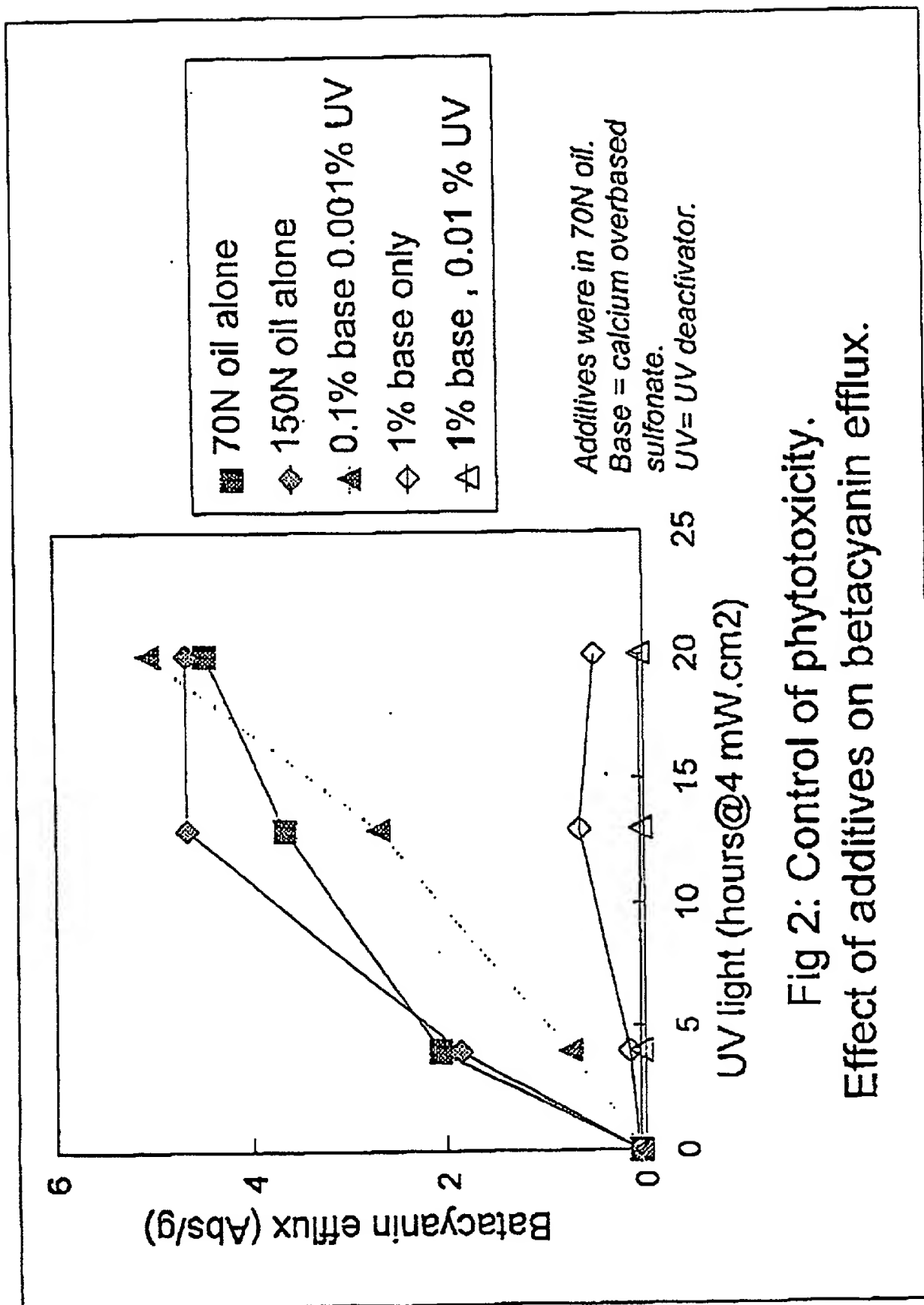


Fig 2: Control of phytotoxicity.
Effect of additives on betacyanin efflux.

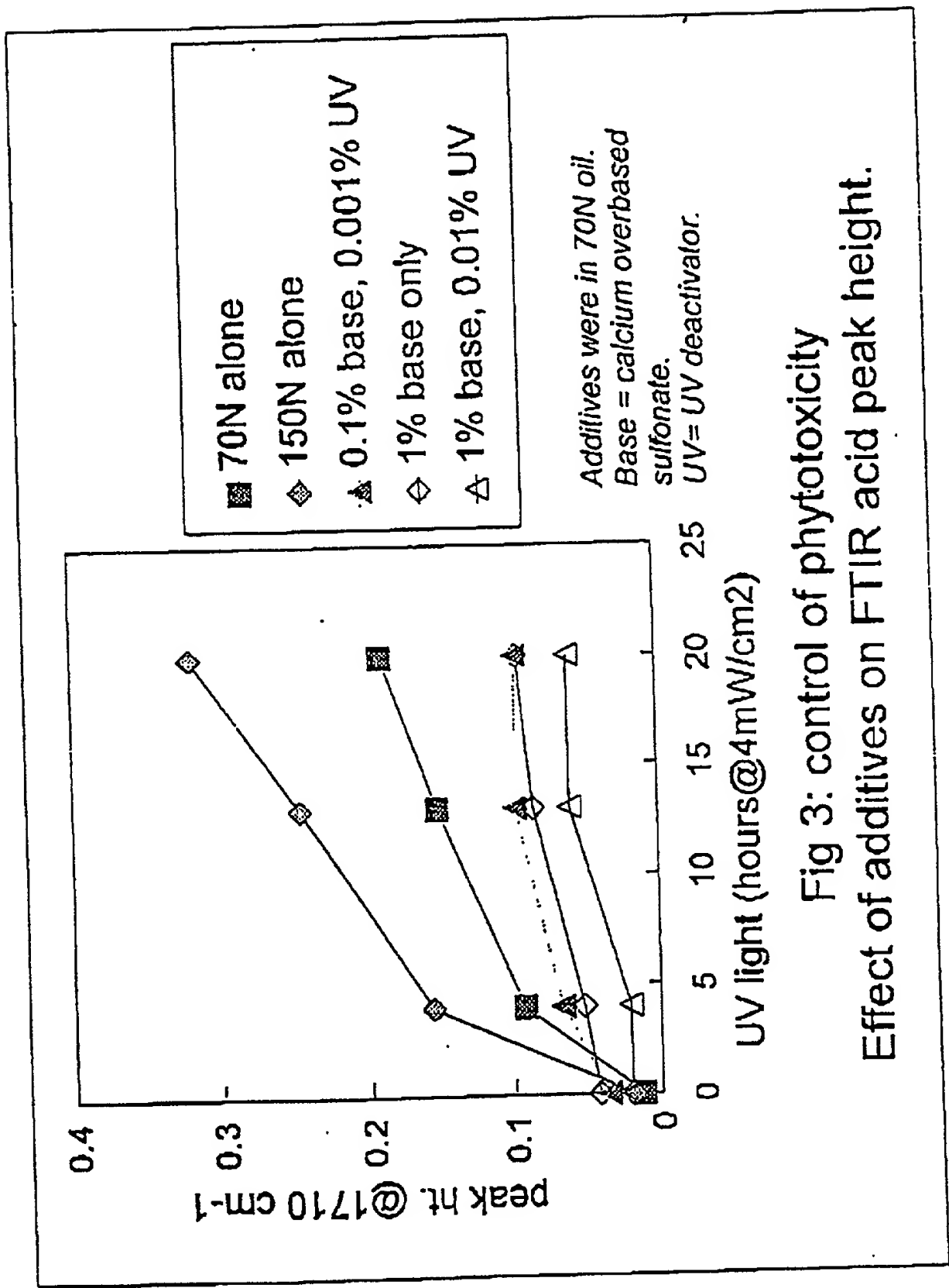


Fig 3: control of phytotoxicity
Effect of additives on FTIR acid peak height.

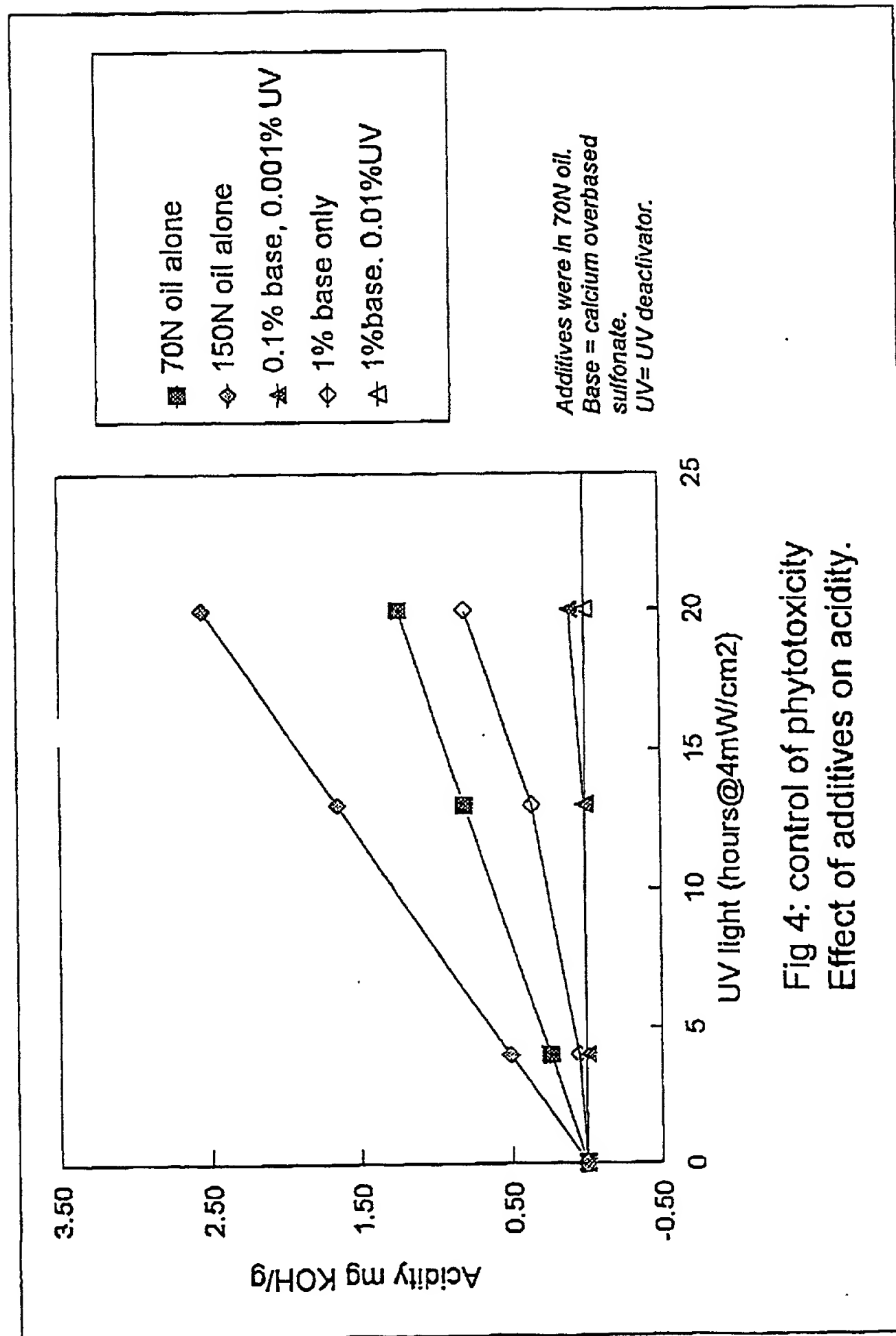


Fig 4: control of phytotoxicity
Effect of additives on acidity.

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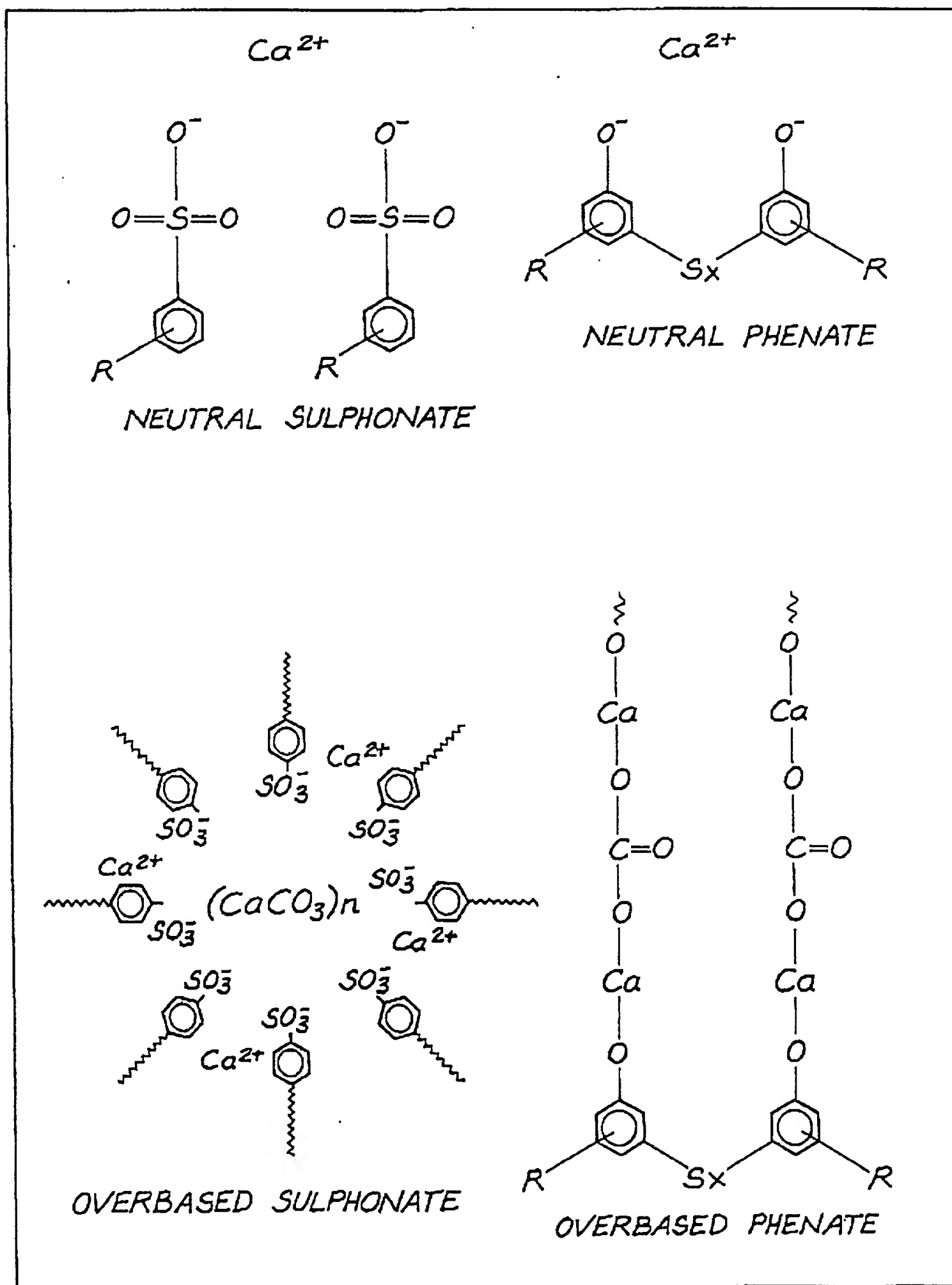
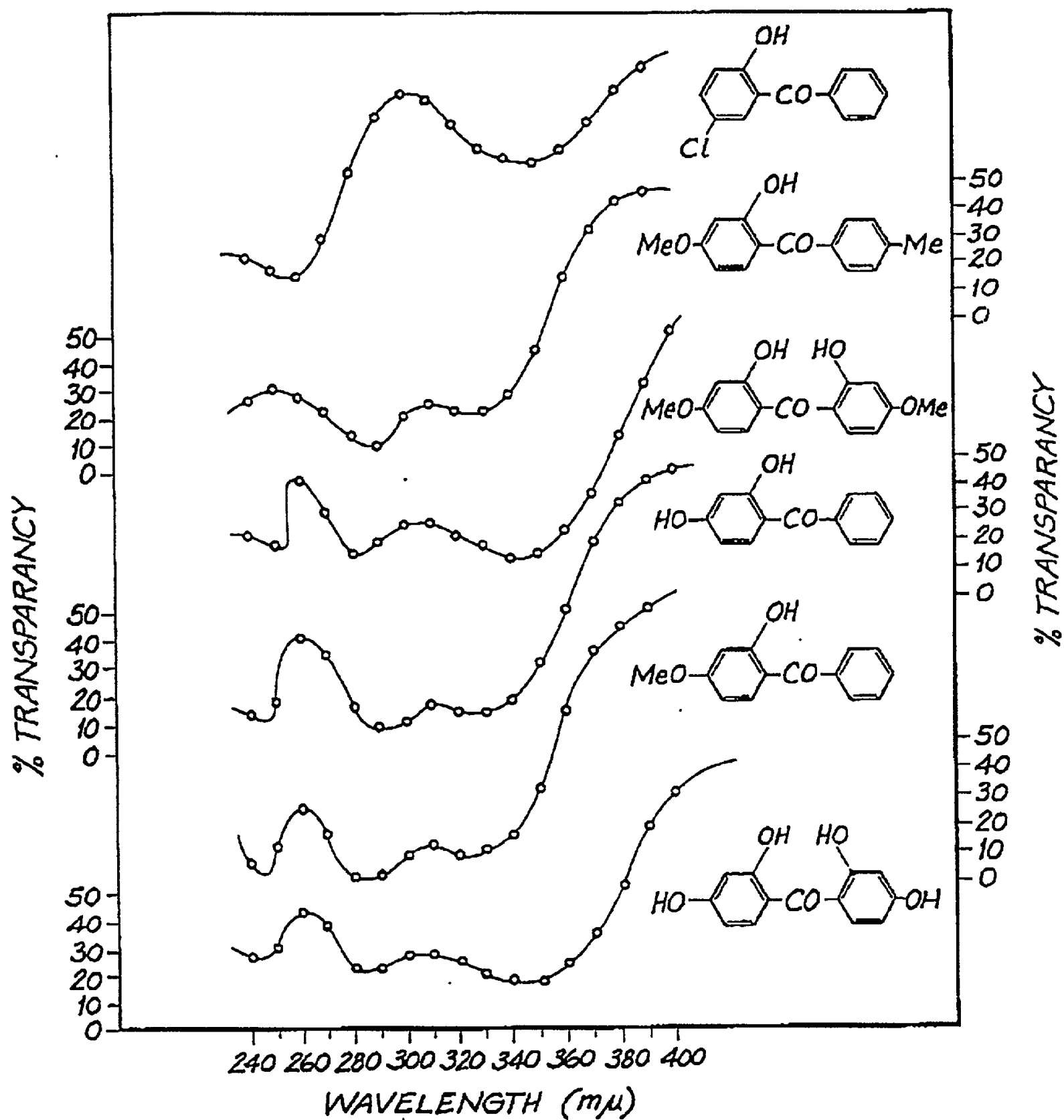


FIG. 5

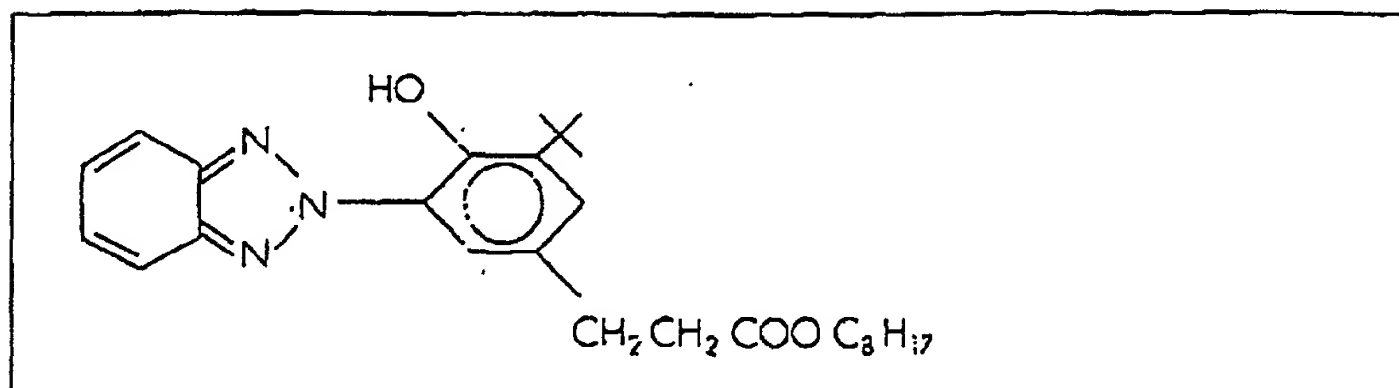
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U.V. ABSORPTION SPECTRA OF TYPICAL
2-HYDROXYBENZOPHENONES

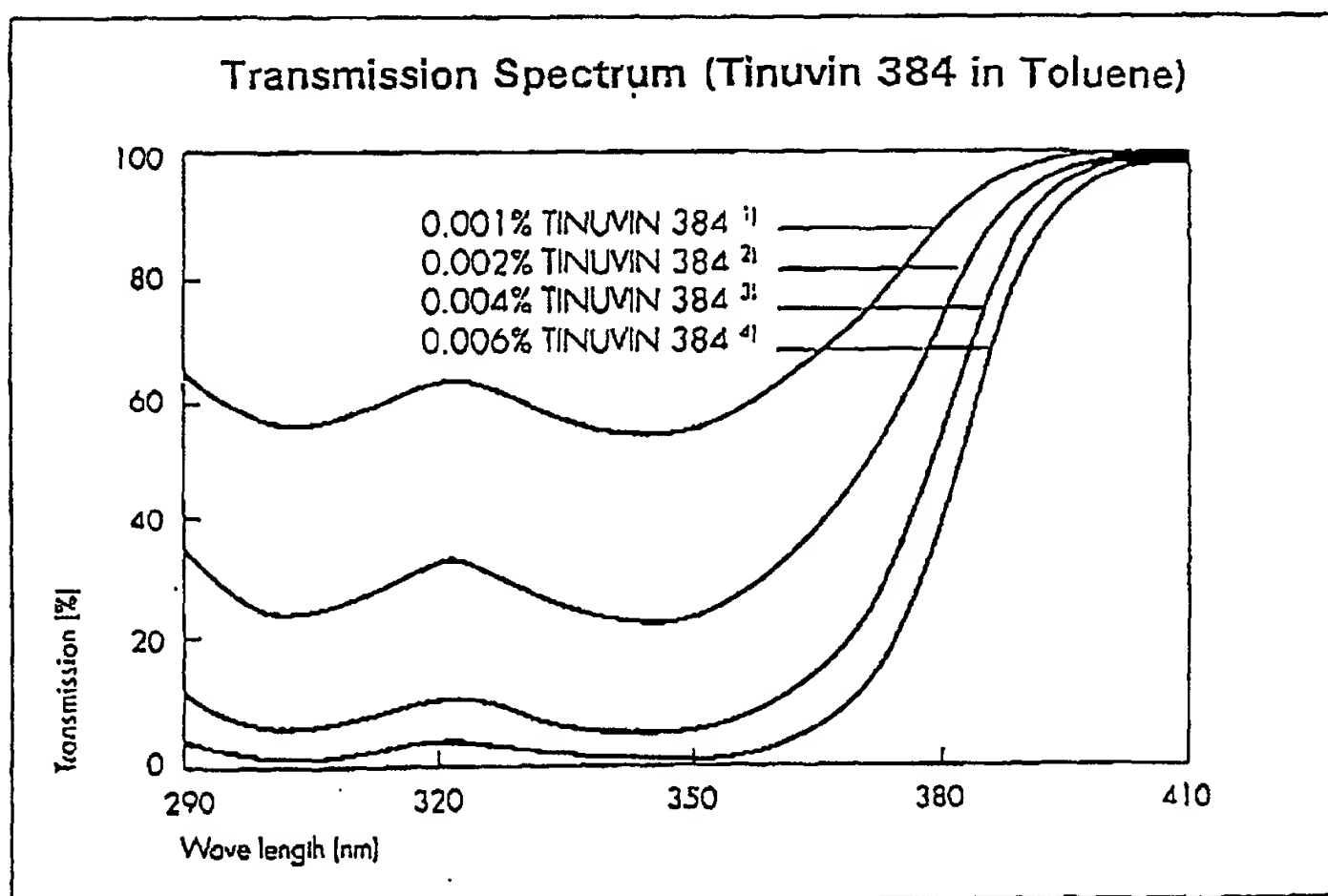
FIG. 6

FIGURE 7



Iso-octyl-3-(3-(2H-benzotriazol-2-yl)-5-tert. butyl-4-hydroxyphenyl)propionate
Molecular weight: 451.6

FIGURE 8



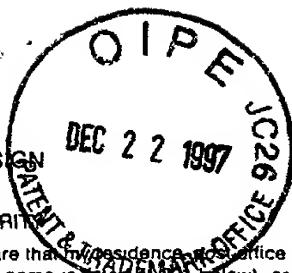
Absorption maximum: 343 nm

¹⁾ corresponds to 0.25% in a 40 μm film

²⁾ corresponds to 0.5 % in a 40 μm film

³⁾ corresponds to 1.0% in a 40 μm film

⁴⁾ corresponds to 1.5% in a 40 μm film



DECLARATION
AND POWER OF ATTORNEY
U.S.A.

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ATTORNEYS' DOCKET NO.

ALL PATENTS, INCLUDING DESIGNS
FOR APPLICATION BASED ON PCT,
PARIS CONVENTION OR NON PRIORITY

As a below named inventor, I declare that my residence, first office address and citizenship are stated below next to my name, the information given herein is true, that I believe that I am the original first and sole inventor (if only one name is stated below), or a first and joint inventor (if plural inventors are named below at 201-203, or on additional sheets attached hereto) of the subject matter which is claimed and for which patent is sought on the invention entitled:

OIL FOR AGRICULTURAL USE

which is described and claimed in:

☒ PCT International Application No. AU96/00189

filed 2 APRIL 1996

☐ the attached specification

☐ the specification in application Serial No. _____

filed _____

(if applicable) and amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specifications, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

PN2187

AUSTRALIA

5/4/1997

☒ Yes

☐ No

(Number)

(Country)

(Day/Month/Year Filed)

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes

☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes

☐ No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status: patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status: patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys (Registration No.) to prosecute this application, receive and act on instructions from my agent, and transact all business in the Patent and Trademark Office connected therewith.

SEND CORRESPONDENCE TO:

DIRECT TELEPHONE CALLS TO:
(please use Attorney's Docket No.)

Inventor(s) name must include at least one unabbreviated first or middle name.

201	FULL NAME* OF INVENTOR	FAMILY NAME HODGKINSON	GIVEN NAME MARK	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY BRISBANE	STATE OR FOREIGN COUNTRY AUSTRALIA	COUNTRY OF CITIZENSHIP AUSTRALIA
	POST OFFICE ADDRESS	POST OFFICE ADDRESS C/- AMFOL, SOUTH ST, LYTON	CITY BRISBANE, QUEENSLAND	STATE OR COUNTRY AUSTRALIA
202	FULL NAME* OF INVENTOR	FAMILY NAME	GIVEN NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY ZIP CODE
203	FULL NAME* OF INVENTOR	FAMILY NAME	GIVEN NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201*	SIGNATURE OF INVENTOR 202*	SIGNATURE OF INVENTOR 203*
DATE 3/19/97	DATE	DATE

☐ Additional inventors are named on separately numbered sheets attached hereto.

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